Nylon 6/Poly($p$-phenylene terephthalamide) 분자복합재료

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Molecular Composites of Nylon 6/
Poly($p$-phenylene terephthalamide)

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Abstract: The melt viscosity and shear thining effect for nylon 6/PPTA blends increased markedly with increasing PPTA content. This is attributed to the existence of solid-like state stiff PPTA molecules or microfibrils. Filaments from the blends were obtained using a capillary rheometer. The PPTA phase in the filament prepared in this investigation exhibited well developed and oriented microfibrillar structure. The storage modulus for nylon 6/PPTA filament increased with increasing shear rate. The tensile modulus and strength of the filaments increased with increasing PPTA content. Higher values of strength and modulus were in part due to the fineness of microfibril and its orientation.

INTRODUCTION

The concept of a rigid-rod molecular composite and a fabrication method was patented in 1980 by Helminiak et al.1 A molecular composite is defined as a mixture of stiff chain and flexible coil macromolecules which is conceptually similar to a fiber reinforced plastics, except that the reinforcement takes place at a microscopic level.2–17 The optimum reinforcement can generally be expected if mixing occurs at a molecular level. The purpose of forming a rig-rod molecular composite is to reinforce a ductile matrix polymer with stiff, strong, rigid-rod polymer molecules. A molecular composite offers advantages over a macroscopic composite(e. g., chopped glass fiber reinforced epoxy) in that
there are no interfacial adhesion problems or thermally induced macroscopic stresses due to differences in thermal expansion coefficient. However, such expectation is difficult to achieve due to the low entropy of mixing and the high tendency of self alignment of the rigid macromolecules. The molecular composites may be thermodynamically unstable and undergo phase segregation either during coagulation or thermal treatment. However, the size of segregated phases in the range of microscopic level in the molecular composites, so their reinforcing effects are better than that of macroscopic composites.

Husman et al. conducted the initial research on the effect of composition on the morphology and mechanical properties of the vacuum cast films of rigid rod poly(p-phenylene benzimidazole) and flexible coil poly(2,5(6) benzimidazole) (ABPBI). They observed that these films were phase separated by SEM, but higher values of mechanical properties were achieved when the dimensions of the rod-rich phase were reduced by more rapid precipitation.

Hwang et al. studied processing of blends of rigid rod poly(p-phenylene benzobisthiazole) (PBT) and ABPBI from homogeneous solution. When solutions were extruded and rapidly coagulated in water, large scale phase separation was prevented. After heat treatment of the fiber or films prepared in the study no phase separation was observed with SEM to its resolution limit of 20nm.

Takayanagi and co-workers have undertaken the studies of morphological and mechanical behavior of the nylon 6/PPTA blend films. They showed that the PPTA phase of the blend films exhibited random microfibrillar structure and the tensile moduli of the blend films were markedly increased with increasing PPTA content. They studied several stiff-chain/flexible coil polymer blends and observed that the finest dispersion in a matrix polymer was microfibrils of 15~30nm in diameter.

Most of the reported works and commercial developments of molecular composite were concerned with tensile strength and modulus, dynamic mechanical properties, and morphology. However, there is no report for the melt behavior of molecular composite.

Consequently, the present study deals with melt behavior of nylon 6/PPTA molecular composite and the properties of filaments prepared by a capillary rheometer. Dynamic mechanical and mechanical properties were obtained with Rheovibron and Tensilon UTM respectively. Optical and scanning electron microscopes were used to examine the morphology of melt and filament of molecular composites. The influences of processing conditions and blend ratio on the texture and properties of the filaments are studied.

**EXPERIMENTALS**

**Materials**

The nylon 6 used in this study was KN171 (Kolon Co., Korea). PPTA was prepared by low temperature polycondensation of p-phenylene diamine and terephthaloyl chloride in a mixed solvent of hexamethylyphosphoramide (HMPA) and N-methylpyrroolidone (NMP). Intrinsic viscosity of the PPTA in 98% sulfuric acid at 25°C was 3.5dL/g. The solvents, HMPA and NMP, were purified by fractional distillation at reduced pressure over calcium hydride and stored over molecular sieves.

**Preparation of Molecular Composite Filament**

The nylon 6/PPTA molecular composites were prepared by pouring the isotropic sulfuric acid solutions of the nylon 6/PPTA blends into a coagulation bath containing a large amount of water. The precipitates were washed with water and methanol. The weight ratios of nylon 6/PPTA for the blends were 97.5/2.5, 95/5, 92.5/7.5, and 90/10. The filaments were prepared by extruding the blend (molecular composites) through a capillary of 1 mm in diameter and L/D ratio of 40 on a capillary rheometer (Instron 3211). The extrusion temperature was 240°C. In order to investigate the effect of drawing on viscoelastic properties, the extrudates were drawn at 195°C on a bench scale drawing.
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apparatus.

**Measurements**

Tensile properties were measured by Tensilon UTM III with a gauge length of 40mm and a strain rate of 5mm/min. at room temperature. Viscoelastic properties, dynamic modulus (\(E'\) and \(E''\)), and \(\tan \delta\) were measured by dynamic viscoelastometer (Rheovibron DDV-II) at 110Hz. The melt viscosity was measured by a capillary rheometer (Instron 3211) with a capillary of 1mm in diameter and L/D ratio of 40 at 240\(^\circ\)C. The optical texture of the blends were observed using a cross-polarized optical microscope. The samples were melted in a thin layer between the cover glasses at 260\(^\circ\)C and quenched to room temperature. The morphology of the filaments were observed by scanning electron microscope. Surface of the filament was etched with 58\%(v/v) formic acid.

**RESULTS AND DISCUSSIONS**

**Morphology**

Figure 1 showed the cross polarized photomicrographs of nylon 6 and nylon 6/PPTA(95/5) blend. Nylon 6 showed a uniform and fine spherulite-like texture. When PPTA was blended with nylon 6, marked birefringent fibrous patterns were observed and no more spherulite-like texture could be found. Takayanagi et al\(^3\) have undertaken the studies of morphological and mechanical behavior of the compressing specimens at 240\(^\circ\)C. They showed that the PPTA phase of the blends exhibited random microfibrillar structure. However, the filaments of nylon 6/PPTA blends prepared by capillary rheometer at 240\(^\circ\)C in this study exhibited oriented microfibrillar structure of PPTA(Figure 2).

**Mechanical Properties**

The stress-strain curves for nylon 6/PPTA blend filaments, prepared by capillary rheometer at 240 \(^\circ\)C, are shown in Figure 3. Takayanagi et al.\(^3\) reported that the nylon 6/PPTA blend films molded at 240\(^\circ\)C exhibited only an increase of modulus. However, for the filament of nylon 6/PPTA blend made here, the strength and modulus increased markedly with increasing PPTA content. Figure 4 shows the stress-strain curves for nylon 6/PPTA (95/5) with various draw ratios. Tensile modulus and strength increased with an increase of draw ratio. This is ascribed to the fineness of PPTA microfibril and their orientation observed in morphology study.

**Dynamic Mechanical Behavior**

Dynamic moduli (\(E'\) and \(E''\)) measured at 110Hz for nylon 6 and nylon 6/PPTA blends made by a capillary rheometer at the shear rate of 365sec\(^{-1}\) at 240\(^\circ\)C and drawn to draw ratio of 2 at 195\(^\circ\)C are
shown in Figure 5. The reinforcing effect of rigid-rod molecule PPTA at supra-molecular level increased sharply with increasing PPTA content up to 5wt% PPTA. Figure 6 shows the effect of draw ratio on the storage modulus (E') and loss modulus (E'') for the nylon 6/PPTA(95/5) filament. Storage modulus increased noticeably with increasing draw ratio. This may be due to the orientation of PPTA microfibril by drawing. The loss factors (tanδ) for

the nylon 6/PPTA(95/5) filament with various draw ratios are shown in Figure 7. The primary tanδ peak shifted to higher temperature with increasing draw ratio. This is probably a reflection of the high orientation of the filament by drawing.

Rheovibron measurement at 110Hz on nylon 6/ PPTA(95/5) filament made at the shear rate of 36, 365, and 1216 sec⁻¹ are shown in Figure 8(E' and E'') and Figure 9(tanδ). Generally, the mechanical properties depend on the arrangement and struc-
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Fig. 6. Dynamic modulus vs. temperature for nylon 6/PPTA(95/5) blends with various draw ratio: (-- 1) as extrudate; (-----) 2; (-- 3) 3; (— 4) 4 draw ratio.

Fig. 7. Tanδ vs. temperature for nylon 6/PPTA(95/5) blends with various draw ratio: (---) as-extrudate; (-----) 2; (-- 3) 3; (— 4) 4 draw ratio.

Fig. 8. Storage modulus vs. temperature for nylon 6/PPTA blends prepared under various shear rate. The shear rates are: (---) 1216 s⁻¹; (-- 365 s⁻¹; (-----) 36 s⁻¹.

Fig. 9. Tanδ vs. temperature for nylon 6/PPTA(95/5) blends prepared under various shear rate. The shear rates are: (---) 1216 s⁻¹; (-- 365 s⁻¹; (-----) 36 s⁻¹.

Fig. 10. Die swell ratio vs. shear stress for nylon 6 (●) and nylon 6/PPTA blends: (▲) 97.5/2.5; (■) 95/5.

ture of polymer chain. The storage modulus for nylon 6/PPTA filament increased with increasing shear rate. This may be due to the order of polymer chain caused by shearing force. Figure 9 shows the influence of shear rate on tanδ for nylon 6/PPTA(95/5) blend filament. The tanδ peak intensity decreased with increasing shear rate.

Melt Behaviors
For the filaments of nylon 6 and nylon 6/PPTA blends made by capillary rheometer at 240°C with various shear rate, die swell was measured (Figure 10). Die swell increased with increasing shear stress, but die swell had lower value as PPTA content increased in nylon 6/PPTA blends. The reason for this may stem from the orientation of microfibrils developed during processing.
at low shear rates. However, the viscosity increased markedly with increasing PPTA content in nylon 6/PPTA blends and shear thinning effect increased with increasing PPTA content. This may be due to the dispersed solid-like state rigid PPTA molecules or microfibril in nylon 6/PPTA blend melt.

Generally, relative viscosity $\eta_r = \mu_r / \mu_0$ (viscosity of composite/viscosity of matrix) observed for composite increased with increasing volume fraction ($\phi$), aspect ratio (length/diameter : L/D), and with the decreasing volume fraction of PPTA at low shear rate (Figure 12). This unusual increase of relative viscosity is attributed to the existence of solid-like state stiff molecules and PPTA microfibril as a reinforcing agent, and to the large aspect ratio of PPTA with microscopic level size.

CONCLUSIONS

The texture and properties of the filaments of nylon 6/PPTA blend (molecular composite) have been studied.

1) The melt viscosity and shear thinning effect for blends increased markedly with increasing PPTA content. This is attributed to the existence of solid-like state stiff PPTA molecules and microfibrils.

2) The PPTA phase in the filaments prepared in this investigation exhibited well developed and oriented microfibrillar structure.

3) The storage modulus for nylon 6/PPTA filament increased with increasing shear rate.

4) The tensile modulus and strength of the filaments increased with increasing PPTA content. Higher values of strength and modulus were in part due to the fineness of microfibril and its orientation.

REFERENCES